Bulk Supply of Cement.

AN account of the method of supplying cement in bulk to a large dam contract in Western Australia is given in a paper read before the Institution of Engineers (Australia) by Messrs. R. J. Dumas and V. C. Munt.

Tests showed that the average amount of cement left in each jute bag, after emptying into a hopper by hand and shaking, was approximately 1½ lb. Over the whole job this would have represented 1,000 tons. In addition, the weight of the bag is also paid for as cement. The cost of the bags, including filling, sewing, tagging, etc., was approximately 9s. per ton. As the result of conferences with the Railway Department a system was evolved resulting in a reduction in railway freight to railhead of 2s. 6d. per ton, and a reduction in road cartage from railhead to dam of 11d. per ton. The bag system entails the employment of men stacking the cement in the sheds, wheeling to the mixers, opening the bags and dumping into the mixer hopper, and collecting, tying in bundles and loading the empty bags for return to the cement works. With the bulk cement and automatic batching, as adopted, the contractor conveys to the dam six tons of cement in bulk, and dumps it directly into the 60-ton capacity steel tank.

The total cost of the bulk cement plant was £1,875, exclusive of cost of containers and railway trucks which were made by the railway department and not charged to the works. This gives a unit cost of 1.32d. per cu. yd. of concrete, or 5d. per ton of cement. The following figures show the savings effected by using bulk instead of bagged cement :—

	Bulk per ton. £ s. d.					Bag per ton. £ s. d.
Capital cost	5	..	..	..	..	—
F.O.R. cement works	3 16 1½	..	..	..	..	4 4 10
Freight	6 2	..	..	..	..	8 8
Cartage	3 4½	..	..	..	..	4 3
Testing fees	1 3	..	..	..	..	1 3
Repairs to containers	1	Sheeting	..	..	..	1
Labour of handling to mixer and repairs	3½	Labour of handling into shed and to mixer	..		2 4
Loss of cement ¼% max...	3	Loss of cement in bags 1%, say,	..	..	..	1 0
Total ..	£4 7 11½	..	..	..	..	£5 2 5

The net saving is therefore 14s. 5¾d. per ton or, say, 3s. 7½d. per cu. yd. of concrete, or a total of approximately £63,000.

Handling Bulk Cement.

The cement manufacturers erected four concrete silos, each of approximately 120 tons capacity, to allow time for the seven-day tests to be completed. Steel containers have been designed so that two can be placed end to end on a standard 3 ft. 6 in. gauge flat-top railway wagon and be readily transferred from it to the chassis of a motor truck. The rectangular design was considered preferable as it enabled the centre of gravity to be kept low while the containers were being transported on the motor chassis, and also because it can be fitted more readily to a motor chassis and emptied by raising one end. The empty container weighs approximately 26 cwt., and up to 6 tons of cement are carried in each container. Two 5-ton trucks have been employed and during ten months these have conveyed an average of approximately 300 tons per week from railhead to dam site, a distance of 11 miles, with practically no breakdowns. A centre opening 18 in. in diameter is provided in the cover-plate of the container, and the cement is filled in through this opening. One end of the container forms a hinged door faced around the edges with a strip of rubber to make a perfect closure when clamped tight.

The cement is conveyed from the foot of the silos by a screw conveyor, raised by a bucket elevator, and delivered through a canvas spout into the containers, which are on railway trucks. Experiments made before the containers were designed indicated that cement filled in this way would not weigh more than 80 lb. per cu. ft. Sufficient volume in the container was therefore provided on this basis. Tests were also made on the angle of repose of cement discharged from a spout, and these indicated that one opening in the top plate was sufficient for filling the containers. The container is transferred at railhead to the motor chassis by an electric gantry which straddles the track. The gantry traverses in a direction parallel to the railway line, and is equipped with twin electric hoists which move in a transverse direction. In this way considerable mobility is obtained, and the transfer is effected in two or three minutes. Each hoist is fitted with a steel bridle and hook, which grapple lugs set at the corners of the containers. The gantry is operated by the drivers of the motor trucks. On the underside of the container, at the discharge end, are two lugs through which two pins from the motor chassis pass. The other end is clamped to the chassis.

The main cement storage bin at the dam is located at the end of a wide timber ramp, with a gantry erected over the bin for the purpose of emptying the containers. The bin, which has a capacity of 60 tons, is 10 ft. square in section for the top 8 ft. and tapers down on three sides over the bottom 14 ft. to an opening 24 in. by 18 in. The bin and gantry are totally enclosed with corrugated iron to ensure weather-tightness, a low entrance shed and doorway giving access to the trucks which are entirely sheltered while tipping is in progress. The

truck is backed along the trestle into position at the front of the bin, and the front of the container is elevated by a friction winch and tackle suspended from the gantry until the container assumes an angle of about 55 deg. with the horizontal.   The rear end of the container pivots on two cast-iron saddle lugs about a shaft attached to the rear end of the chassis.   The clamps on the door at the back are previously unfastened, and as the front of the container is raised the door swings open and the cement is delivered into the bin.

In the original design the cement was then fed through a door in the bottom of the bin into the boot of a vertical bucket elevator which delivered it through a 12 in. diameter pipe, on an incline of 52 deg., to a secondary bin of 2.5 tons capacity located above the mixer.   The rate at which the elevator was to be fed was to be regulated by the adjustment of the door, which moved horizontally between guides and was fitted with a hand wheel and rack and pinion gearing. It was here that the lack of experience led to the first difficulties.   In the first place the cement was found to be so fluid that it discharged through the smallest of pin holes in the welding at the corners of the bin and squeezed out between the door and the door guides.   The welding was caulked and a baffle welded to the door to prevent the escape of cement in this way.   It was found that a door-opening of an inch or two gave the required rate of feed for a time but the cement then formed an arch above the door and this arch had to be broken before feeding of the elevator could continue. · Breaking of the arch by increasing the door opening resulted in the flooding of the boot to such an extent as to prevent the operation of the elevator.   Each flooding meant a considerable waste of time and labour, as a portion of the casing had to be removed and the cement scraped out and bagged.   This operation took nearly three-quarters of an hour.

To prevent the formation of the arch the first step was the installation of a chain agitator, which consisted of an endless $\frac{3}{4}$-in. chain suspended in the cement from the top of the bin to within about 6 in. of the door, and driven through gearing by a 7-h.p. motor.   It was found, however, that the chain could not be made to re-enter the surface of the cement and merely worked upwards leaving the arch unbroken.   It was then decided to fit compressed air jets to the sides of the bin above the door to prevent arching by keeping the cement agitated. In the first test, six $\frac{3}{8}$-in. diameter jets were placed on two sides of the bin about 12 in. above the door and connected to the air line, but the arch continued to form and seven more jets were placed in the sloping back to a height of 8 ft. above the door.   The consequent aeration of the cement in the vicinity of the jets meant that the door opening had now to be reduced to about $\frac{1}{8}$ in. to prevent flooding.   This opening gave the required rate of feed for about half an hour, when the opening became blocked by the accumulation of cement on its edges. The door had then to be opened wider and greater flooding occurred.   It was then found that, although the cement near the jets was more fluid than before, the cement above the jets was unaffected and the arch formed higher up, even though the air bubbled the cement to the top of the bin.   A $\frac{1}{2}$-in. air pipe was therefore led into the cement from the surface to within a few feet of the door, but the arch remained unbroken.

After the shape of the door had been altered by the insertion of check plates in the sides and front of the bin, without success, it was thought that the formation of the arch might be prevented by continued hammering of the exterior of the bin. An air gun of the type used in scabbling, fitted with a flattened tool, was mounted in such a position as to operate against the bin at the spot where the arch formed. This met with more success, but the effect on the bin was far from beneficial and there was no certainty about its action. Flooding still continued on the breaking of the arch, and the method was abandoned after a time.

It was then decided to modify the design of the plant in an endeavour to rectify the trouble. The direct method of feeding under gravity from the main bin to the elevator boot was abandoned and the shape of the bin at the bottom was altered to allow of the installation of a short screw conveyor, which forced cement from the bin horizontally to the boot. It has now been in operation for some months and has proved satisfactory. The door is left open to its full extent, thus reducing the chance of an arch forming, and the conveyor feeds at a constant rate irrespective of any flooding from the bin.

From the elevator boot the cement is hoisted vertically in buckets attached at 18-in. centres to a 10-in. wide canvas belt carried on head and tail pulleys and driven by a 7-h.p. motor. The elevator is housed in a mild steel casing. The buckets discharge at the head of the elevator into a 12 in. diameter pipe, through which the cement gravitates to the small bin. From this bin it is drawn off through a second door to the batching hopper, where the required batch is weighed and passed to the mixer. Should a blockage occur in the 12-in. pipe, backflooding of the elevator is prevented by an overflow pipe which takes off well below the elevator head and by-passes the cement back to the main storage bin.

The door connecting the secondary bin and the batching hopper, when first installed, also gave considerable trouble. It was a flat plate door moving horizontally between guides, and operated automatically by compressed air. Considerable leakage occurred between the door and the opening, and although efforts were made to prevent this by means of rubber insertion and other means, little success was achieved. The door now in use consists of a horizontal cylinder in which a piston moves back and forth to open or close a circular shaft passing through the vertical axis of the cylinder. A second piston, joined to the first by a distance-piece, moves forward with it, and when the door is open the two pistons, one on each side of the opening, prevent the escape of cement through the cylinder. Cement lodging in the clearance between the pistons and the cylinder forms a gasket and prevents further leakages.

M. Freyssinet's Process of Making High-Strength Concrete.

IN our last issue we gave an abstract of a paper by M. E. Freyssinet in which the author describes his new process by which very high strengths are obtained in ordinary Portland cement concrete a few hours after placing the material. Two British patents have been granted to M. Freyssinet in respect to the appli-
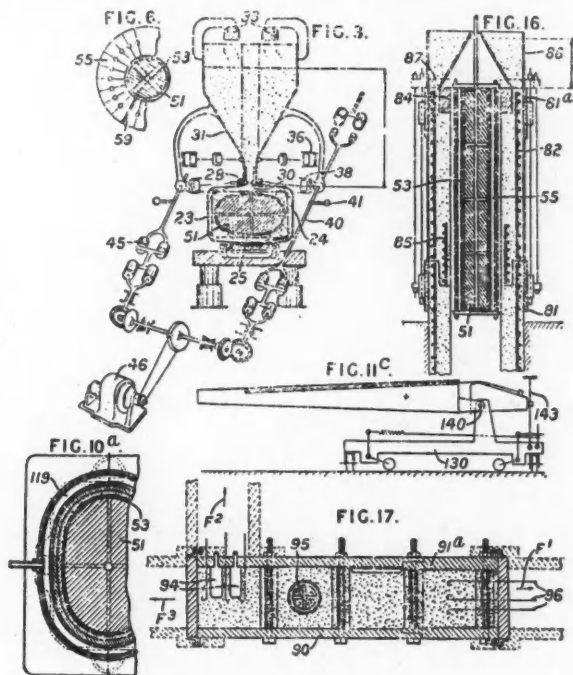
MOULDING CONCRETE IN SITU.

cation of the process in the manufacture of pre-cast concrete articles and for *in situ* work. Abstracts of these patent specifications are as follow.

Moulding Concrete in situ.

(Patent No. 431,484, 1934).—Articles are moulded from damp concrete by filling a non-rotary mould with concrete which is subjected in a first phase to vibration accompanied by pressure applied to the upper portion of the concrete ; the pressure coacts with the vibration to produce compactness, but is not strong enough to prevent relative displacement of the elements of the concrete. During

a second phase the compact concrete is subjected to a substantially greater compression, preferably obtained by reducing the size of the mould.

As shown in *Fig.* 3 the mould comprises two elements (23, 24) having a lower joint (25) filled with yielding packing, for instance, perforated wood, to allow water to leak out. The upper edges (28) of the elements are pressed against the lower end of a hopper (31) by jacks (38) and have rubber lips (30) which can be closed by jacks (36). The hopper is supported on rubber parts (33) and is vibrated by excentric masses (41) on shafts (40) which are driven through flexible couplings (45) from a motor (46). The amplitude and energy of the vibration may be regulated by varying the excentric masses and their speed of revolution.

The concrete remaining in the hopper when the mould is full supplies the preliminary pressure required, and excess water rises to the upper part of the hopper, thus rendering the concrete in the mould homogeneous. When the mould is full the hopper is removed, the joint (28) is closed by a wooden or metal plate, and a second strong compression is supplied by an expanding mandrel (51). The vibration may be produced by rotating excentric masses inside the mandrel. The first pressure may be applied directly to the concrete by various devices, such as a wooden or felt plug held down by a screw, a leaky joint maintained by an elastic member, a hydraulic plunger, a floating weight, or an inflated rubber bag. A concrete pump may also be used for filling the mould and applying pressure.

The expanding mandrel may comprise a rigid core (51) of wood or metal surrounded by a rubber envelope (53) reinforced by fabric, which is inflated by fluid. The envelope (53) may be held in contact with the core (51) at its edges by means of an inflated tube (119). In a modification (*Fig.* 6) the elastic envelope (53) is surrounded by a system of staves (55) of steel, wood, or synthetic resin. When the envelope (53) is expanded water can escape through the cracks between the staves, these cracks being covered on their inner ends by pieces of metal, wood, or rubber, or by wire mesh. A steel wedge (59) may be provided which is driven inwards to facilitate withdrawal of the core. The core may be supported on a wheeled carriage (130, *Fig.* 11c), the core being pivoted at 140 and actuated by a screw (143). Several expanding mandrels may be placed in the mould near the centre or on the periphery. In place of these mandrels the mould may be made in two parts which are moved together by a jack or inflatable bag. The vibratory treatment may, in some cases, be continued during the second compression.

Aluminous cement or Portland cements may be used and, in order to shorten the time of hardening, the material may be progressively heated from 15 to 90 deg. C., the surrounding medium being kept at a slightly higher temperature by water vapour so as to avoid too rapid dehydration. Some time may elapse between the mixing of the concrete and filling the mould or between the two steps of the process in order to hasten the hardening.

Piles may be manufactured in successive portions as shown at *Fig.* 16. The

mould (82) is connected by an element (81) to a previously-formed portion of the pile and an expansible mandrel (51) is placed inside, the mandrel having an annular projection (84) at the top end to form a recess in the concrete.   Reinforcements (85) are placed in the mould, which is filled by a hopper (86), the material in which provides light pressure.   The mould is vibrated by rotating excentric masses.   The hopper is then removed, a closure plate (87) is applied, and the mandrel (51) is expanded by fluid pressure.   When the mould is removed the end element (81a) is left in position.   The method is particularly applicable to screwed piles.

Fig. 17 shows the construction of large monolithic elements, such as beams and arches.   The mould comprises wall elements (90) which are vibrated and also elements (91a) which adhere to the concrete.   The concrete element shown can be continued in the directions F^1, F^2, F^3, and cores (94) are provided for housing connecting reinforcements, elastic cores (95) being also provided for compressing the concrete.   The successive elements are connected by projecting reinforcements (96) which may be joined by autogenous welding.
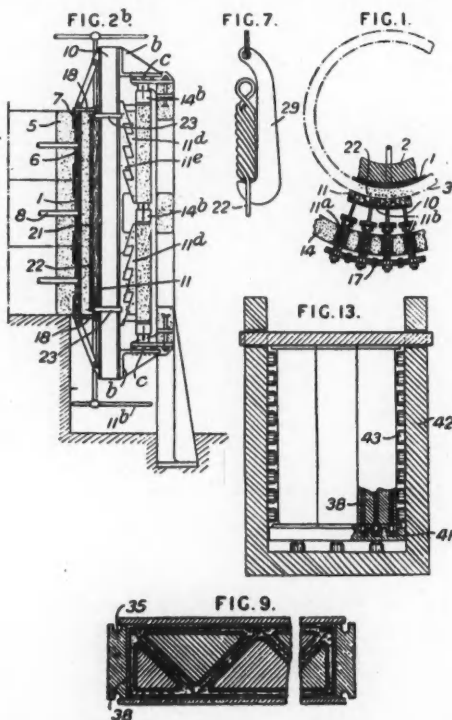
Manufacture of Pipes and Piles.

(Patent No. 433,059, 1934).—In the manufacture of hollow bodies from reinforced concrete, the moist concrete, together with non-rectilinear reinforcements, is placed between a deformable mould and a deformable mandrel, the concrete being first subjected to vibration or moderate compression, or the two combined, to eliminate excess water and then being subjected to a strong compression by expansion of the mandrel to tension the reinforcements and expand the mould, the article being removed from the mould when the concrete is sufficiently hard to resist the tensioned reinforcements.

The apparatus comprises a central mandrel having a rigid core (2) surrounded by a rubber envelope (1) and an outer mould (3).   The core (2) may comprise concrete rings (5) surrounded by metal sheets (6).   The envelope (1) is reinforced by longitudinal rods and is connected to the sheets (6) at its edges by rubber rings (7).   The mould (3) comprises a series of wooden staves (11) impregnated with synthetic resin and supported by section irons (10) which are held in position by screw jacks (11a) in an outer frame (14).   Longitudinal reinforcements (22) are first fixed in the mould by pins (23) and subjected to tension by twisting their ends together in pairs as shown in *Fig.* 7 and tensioning them by tools (29) before the pins (23) are inserted.   Circular hoops (21) are then wound around the reinforcements (22) and an annular hopper is attached to the top of the mould. The mould is filled with moist concrete and vibrated by applying shocks to the irons (10) and also by producing a vibratory injection of fluid into the envelope (1) through the tubes (8) so that the excess water is evacuated through the staves (11) or rises into the hopper.   The hopper is provided with knives for striking off excess concrete from the mould and, after its removal, lids (18) are clamped on. Fluid under pressure is then admitted to the envelope (1) and the jacks (11a) are unscrewed by racks (17) so that the mould may expand and the reinforcements (21) may be tensioned.

To accelerate the setting of the concrete it may be heated by pipes (11*b*). When the concrete has set the jacks (11*a*) are fully unscrewed and the moulded pipe is removed vertically.

In a modification (*Fig. 2b*) the screws (11*a*) are replaced by wedges (11*d*) which co-operate with similar wedges (11*e*) on the irons (10) to adjust the size of the mould under the action of hydraulic jacks (14*b*). The irons (10) are supported by angle members (*b*) which roll on rollers (*c*) on the frame.

MANUFACTURE OF PIPES AND PILES.

In another modification, the irons (10) may be surrounded by a second elastic envelope inside a rigid outer frame and containing fluid under pressure. When the pressure in the core is increased above the pressure in the outer envelope the mould expands. When making hollow bodies for floors (*Fig.* 9) the mould has movable side walls (35) and a number of mandrels (38). The longitudinal reinforcements are tensioned by gripping members (41), and the moulds are stacked in a frame (42). Jacks (43) bear against the mould walls, and the moulds are first filled and vibrated and the concrete is then compressed by expanding the mandrels (38). On releasing the jacks (43) the mould expands and tensions the transverse reinforcements.

Research on Cement.

THE following abstracts dealing with research on cement and concrete carried out at the Building Research Station are taken from the report for the year 1934 of the Department of Scientific and Industrial Research.

The System Lime-Alumina-Silica-Ferric Oxide.

Portland cement is produced by burning the raw materials to a clinker at a temperature such that 20 to 30 per cent. of the mix becomes liquid. The mix is to be regarded as approaching closely to equilibrium at the clinkering temperature though differing slightly from it in that a small amount of lime may fail to combine and may remain present in the free state. There are, however, strong grounds for considering that the equilibrium between the liquid and solid present at the clinkering temperature is " frozen " from this point on cooling, and that the cooled clinker may therefore be regarded as made up of two separate systems produced respectively from the solid and liquid phases present at the clinkering temperature. The content of the various compounds present in the cooled clinker are found, on application of this conception, to differ appreciably from those calculated in the manner described by Bogue[1] on the assumption that the cooled clinker is in complete equilibrium. Three possibilities have now to be considered :—The liquid present at the clinkering temperature may fail to crystallise on cooling and may form a glass ; it may crystallise completely ; or only partial crystallisation may occur. Methods have been worked out, and expressed in the form of equations, for calculation of the compound contents of cements for the two extreme conditions. These equations, which are recorded in a Technical Paper[2] may be further simplified by introducing suitable approximations and may be expressed, in a form most convenient for use, as deviations from the values obtained by the Bogue method. These approximate deviation formulæ do not involve the lime or silica content of the mix and depend only on the alumina and ferric oxide content. The magnesia and alkalis present in cements must also have some small effect, but it seems unlikely that the differences will be large. The approximate deviation formulæ are also affected somewhat by the clinkering temperature, but again, with rare exceptions, the differences will not be large. If the Al_2O_3 content of a cement is X per cent., and the Fe_2O_3 content Y per cent., the compound content of a cement deviates from the Bogue values approximately by the amounts given by the formulæ shown below. The two cases considered are, (a) the liquid present at the clinkering temperature crystallises completely, and (b) it fails to crystallise and forms a glass.

(a) When the liquid crystallises independently on cooling the Bogue values are correct for cements with Al_2O_3/Fe_2O_3 ratios between 0.9 and 1.7. From

[1] Bogue, R. H., Calculation of the compounds in Portland cement. *Ind. Eng. Chem., Analytical Edition,* 1929, **7** (4), 192–7. (*B.S.A.,* 1930, No. 88.)

[2] Lea, F. M., and Parker, T. W., The quaternary system $CaO–Al_2O_3–SiO_2–Fe_2O_3$ in relation to cement technology. *Building Research Technical Paper No.* 16. London, 1935. H.M. Stationery Office.

ratios of 1.7 to 6.1 the corrections to be added to values obtained from the Bogue method are

$$3CaO.SiO_2 \qquad + (1.8\ X\text{--}2.8\ Y)$$
$$2CaO.SiO_2 \qquad + (2.1\ Y\text{--}1.4\ X)$$
$$3CaO.Al_2O_3 \qquad + (2.5\ Y\text{--}1.6\ X)$$
$$5CaO.3Al_2O_3 \qquad + (1.2\ X\text{--}1.8\ Y)$$
$$4CaO.Al_2O_3.Fe_2O_3 \qquad \text{Nil.}$$

(b) The clinker liquid normally contains all the alumina and ferric oxide present in the mix, as well as some lime and silica.   When this liquid fails to crystallise the aluminate and iron compounds are replaced by a glass.   The amount of glass formed is $2.95\ X + 2.2\ Y$.   This formula gives the glass produced from the CaO, Al_2O_3, SiO_2 and Fe_2O_3 constituents.   In commercial cements it is increased by the magnesia and alkalis present by an amount of the order of the total content of these minor constituents.   The additive corrections to the Bogue values for the silicate constituents are

$$3CaO.SiO_2 \qquad + (1.8\ X\text{--}2.8\ Y)$$
$$2CaO.SiO_2 \qquad + (1.9\ Y\text{--}2.1\ X)$$

for all Al_2O_3/Fe_2O_3 ratios from 0.9 to 6.1.

It is not possible at present to determine with any certainty the extent to which the clinker liquid has crystallised on cooling, nor is the extent known to which variations in this factor affect the properties of cement.   It is possible to show from an analysis of the results of the phase equilibrium work that the maximum amount of lime which can be combined under clinkering conditions in a mix of CaO, Al_2O_3, SiO_2, Fe_2O_3 of Portland cement composition is given by the formula

$$\text{Maximum CaO} = 2.80\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3$$

where the amounts of the oxides are represented as weight percentages.   Though this formula cannot apply precisely to commercial Portland cements, since it ignores certain minor components, it may be expected to be adequate for practical purposes.

Hydrated Calcium Silicates.

The study of hydrated calcium silicates has been continued.   The hydrated monocalcium silicate ($CaO.SiO_2.xH_2O$) has been prepared in a fairly pure state by (1) precipitation from sodium silicate solutions by calcium nitrate and lime water; (2) allowing finely-divided silica gel and lime to react for long periods and extracting the excess lime at concentrations above the hydrolysis point ; and (3) hydration of tricalcium silicate at ordinary temperature and extracting the excess lime as in (2).

The material is in every case an amorphous substance with the properties of a gel.   Its water-content-vapour-pressure relationships and other properties are being examined.   The isolation of the compound formed at high lime concentrations is attended with some difficulty, but attempts are being made to isolate it in a pure state.

The hydration of tricalcium silicate and dicalcium silicate at high temperatures in steam yields compounds very different from those formed at ordinary temperatures. The compounds formed are in both cases crystalline and have somewhat similar refractive indexes. It has been found that free calcium hydroxide is not formed in either case, and therefore a hydrate or hydrates of tricalcium silicate must be formed. This is confirmed by the X-ray powder diffraction patterns, which are distinctive and do not indicate the presence of any appreciable proportion of calcium hydroxide.

The relative stability of these compounds is of considerable interest. The hydrated silicate existing in saturated lime water at ordinary temperatures is very readily decomposed to hydrated monocalcium silicate and lime ; the hydrated monocalcium silicate dissolves in water but the solubility is very low. The hydrated tricalcium silicate and hydrated dicalcium silicates formed by autoclaving are, however, despite their comparatively high lime content, relatively stable. In both cases there is very little decomposition in half-saturated lime water when shaken for periods of up to one month, although slow progressive solution occurs, showing that the condition is really a metastable one.

Specification Tests for Pozzolanic Cements.

The tests in use in the specification testing of Portland cement require modification and extension before they can be considered satisfactory for application to pozzolanic cements. The strength of a pozzolanic cement made by blending a pozzolana and a Portland cement will, at the early ages used in specification testing, depend mainly on the proportion and rate of hardening of the Portland cement present in it. The ultimate value of such a cement for the uses to which it will be put will depend on the quality and content of the pozzolana present. It is desirable, therefore, that in addition to strength tests specifications for pozzolanic cement should contain some test which evaluates the content and quality of the pozzolana present. The omission of such a test from Continental specifications for pozzolana cements is an indication that a test of this nature, suitable for use in a specification, has not been easy to find.

Since the value of a pozzolana in a pozzolanic cement in contributing to the strength development at long ages, and to the increased resistance to sulphate waters which is developed, is connected with its reaction with the free calcium hydroxide liberated in the set Portland cement, it seems that in some rapid measure of this action there may lie the most effective test of the quality and amount of a pozzolana present in a blended cement. Tests are in progress with a pozzolanic cement gauged neat with water to a defined consistency, cured for 3 days in moist air at 16–17 deg. C. followed by 4 days in water at 50 deg. C. The specimen is crushed and the amount of lime is determined which can be extracted by shaking in a given manner with half-saturated lime water. The amount of lime which can thus be extracted seems likely to afford some index to the value of the pozzolana present in the cement.

Heat Evolution of Concrete.

Tests have been carried out on concrete prepared from many different brands of Portland cement and cured under conditions of complete insulation. Observations have been made of the rise in temperature and the strength development under such conditions. In *Fig* 1 a comparison is made between the crushing strength of concrete cured under normal conditions, i.e., 17 deg. C. and that completely insulated. The tests, which were made on more than thirty batches of Portland cement, show that although two cements may produce concrete of similar strength under normal curing conditions, the strength may be very different when cured under the conditions of complete insulation. For example, two samples of concrete having a strength of 1,000 lb. per square inch under normal
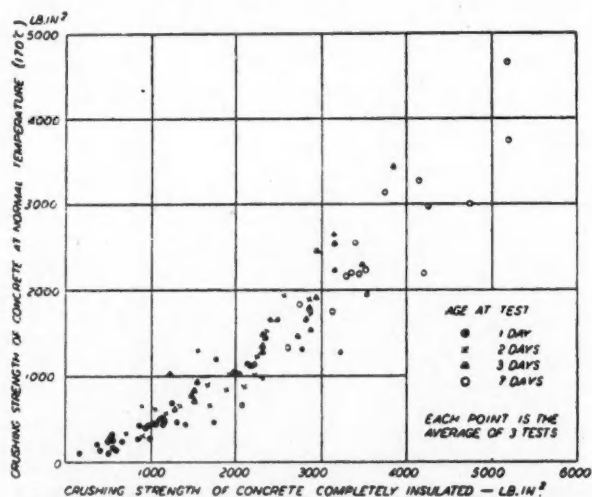
Fig. 1.—Relation between crushing strength of concrete cured normally at 17° C. and under complete isolation (1 : 2 : 4 mix, 0.6 water-cement-ratio. Proportions by weight).

conditions may have individual strengths when cured under insulated conditions of about 1,200 and 2,400 lb. per square inch.

In *Fig.* 2 the rise in temperature of the concrete after placing is plotted against the crushing strength when cured under completely insulated conditions. The very big difference in the behaviour of the different batches of cement is again apparent ; two samples of concrete, although both having a temperature rise of, say, 30 deg. C. after placing, may have strengths as widely divergent as 1,500 and 3,500 lb. per square inch. The graph also shows that a rise in temperature of about 10 deg. C. occurs after placing with this particular mix of concrete (1 : 2 : 4 : 0.6 by weight) without any appreciable development of strength.

Fading of Concrete Products.

The loss of colour of concrete products may be due to one of several causes : (1) deterioration of the pigment, (2) sulphate attack by highly-polluted atmospheres, (3) efflorescences of soluble salts, or (4) formation of insoluble films of calcium carbonate.

Investigations have been proceeding on the factors affecting the formation of calcium carbonate films and, while the work is as yet only in its early stages, some interesting results have been obtained. The effect of soluble salts on the formation of these films has proved to be most striking. Normal Portland cement contains only a small proportion of soluble constituents other than lime, but, as concrete dries out, these salts tend to concentrate at the surface and the liquid
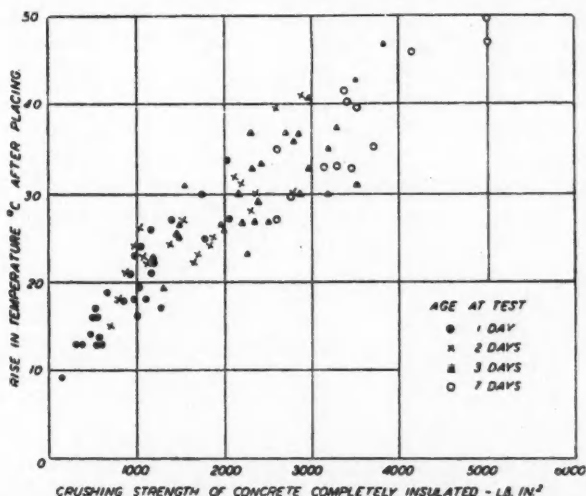
Fig. 2.—Relation between rise in temperature and crushing strength of concrete under conditions of complete insulation (1 : 2 : 4 mix, 0.6 water-cement-ratio. Proportions by weight).

there may contain relatively high concentrations of soluble salts. The addition of one-half per cent. of alkalis to an alkali-free cement resulted in a very marked breaking up of the continuity of the carbonate fade film, while the presence of sulphate was found to increase its continuity.

When certain substances were added, although there was no diminution in the extent or thickness of the surface film, the physical form of this film was so modified that there was no apparent fade. There is as yet no evidence that such " invisible " films can be produced in normal exposure or that a cure for fading will result from their production, but the results appear to be worth pursuing.

The influence of drying conditions and the effect of surface waterproofers have also been studied.

Effect of Calcium Fluoride on Thermal Synthesis of Calcium Ferrites.

By S. NAGAI and T. YOSHIURA.

In a paper presented recently to the Institute of Silicate Research, Tokyo Imperial University, the authors state :—

One of the present authors (S. Nagai) has already reported the results of studies on the effect of calcium fluoride on the thermal synthesis of calcium silicates[*] and the effect of calcium fluoride on the thermal synthesis of calcium aluminates[†]. The present report gives the results of studies on the effect of calcium fluoride on the thermal combination of lime and ferric oxide with calcium ferrites.

Pure calcium carbonate and ferric oxide were intimately mixed in the ratio of two molecules of lime to one molecule of ferric oxide, i.e., $2CaCO_3 : Fe_2O_3$ or $2CaO : Fe_2O_3$. This raw mixture is described as $2CaO : Fe_2O_3$ (2 : 1). Two kinds of calcium ferrites and two kinds of raw mixture, i.e. $2CaO : Fe_2O_3$ (2 : 1) and $CaO : Fe_2O_3$ (1 : 1), have to be prepared to study the problem. It had previously been observed that monocalcium ferrite $CaO.Fe_2O_3$ had a relatively lower heating temperature than a raw mixture of higher lime content $2CaO : Fe_2O_3$ (2 : 1), so it was sufficient to study the mixture with the higher lime content.

The raw mixture was heated in a platinum crucible at 900 to 1,300 deg. C. for one hour in an electric tube furnace. The heated product was analysed with 0.1 N-HCl solution to determine the amount of dicalcium ferrite $2CaO.Fe_2O_3$ produced ; the 0.1 N-HCl solution was found to be too weak to dissolve $2CaO.Fe_2O_3$ completely ; 0.2 N-HCl solution was also too weak, but 0.3 N-HCl solution was just strong enough to dissolve $2CaO.Fe_2O_3$ only and to separate it from monocalcium ferrite $CaO.Fe_2O_3$ and free uncombined ferric oxide in the form of insoluble residue, which can be analysed by fusing by the ordinary method.

The heated product was treated as follows : (1) Free lime was determined by the titration method of Lerch and Bogue ; (2) the amount of $2CaO.Fe_2O_3$ produced was determined by dissolving with 0.3 N-HCl solution ; (3) the residue from (2) was fused with fusion mixture, dissolved in HCl, and the amounts of CaO and Fe_2O_3 determined, from which the amounts of $CaO.Fe_2O_3$ and free uncombined Fe_2O_3 were calculated ; (4) the molecular ratio of total combined lime to total combined ferric oxide was calculated from the results of (2) and (3) ; and (5) the specific gravity of the heated product was determined. The results are given in Table I.

It is seen that (1) Monocalcium ferrite $CaO.Fe_2O_3$ was produced at 1,000 to 1,100 deg. C. even from the raw mixture $2CaO : Fe_2O_3$ (2 : 1) of high lime content, (2) Dicalcium ferrite $2CaO.Fe_2O_3$ was produced gradually at the lower heating temperatures, but the complete combination was attained by heating at 1,200 deg.

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[*] *Cement and Cement Manufacture*, May, 1932 ; October, 1933 ; January, 1934 ; April, 1935 ; September, 1935.
[†] *Cement and Cement Manufacture*, June, 1932.

TABLE I.—SYNTHESIS OF CALCIUM FERRITES FROM THE MIXTURE $2CaO : Fe_2O_3$ $(2 : 1)$ BY HEATING AT 1,000 TO 1,300 DEG. C. FOR ONE HOUR.

Temperature, Deg. C.	1,000	1,100	1,200	1,300
Free lime, %	34.29	21.64	0.57	0.23
Total dissolved lime, %	37.10	35.24	40.80	40.88
Com- ⌠ CaO of $2CaO.Fe_2O_3$, %	2.81	13.60	40.23	40.65
bined ⌡ CaO of $Cao.Fe_2O_3$, %	3.33	6.55	0.04	0
lime Total, %	6.14	20.15	40.27	40.65
Combined lime, %				
Total lime, %	15.2	48.2	98.6	99.5
Uncombined ferric oxide, %..	32.28	17.04	1.43	1.03
Fe_2O_3 insoluble in 0.3 N-HCl, %	41.77	35.70	1.54	1.0
Com- ⌠ Fe_2O_3 of $2CaO.Fe_2O_3$, %	16.68	22.48	56.78	57.90
bined ⌡ Fe_2O_3 of $CaO.Fe_2O_3$, %	9.49	18.66	0.11	0
Fe_2O_3 Total, %	26.17	41.14	56.89	57.90
Combined Fe_2O_3, % ..				
Total Fe_2O_3, %	44.8	70.7	97.6	98.3
$CaO.Fe_2O_3$, %	13.0	25.2	0.2	0
$2CaO.Fe_2O_3$, %	19.7	36.1	97.8	98.8
Total, %	32.7	61.3	98.0	98.8
Molecular ⌠Combined CaO ⌠ soluble in 0.3 ratio of ⌡Combined Fe_2O_3 ⌡ N-HCl	0.48	1.72	2.02	2.00
Specific gravity of heated product	4.15	4.17	3.97	3.97

C., and (3) the high specific gravity of the mixture $2CaO : Fe_2O_3$ $(2 : 1)$ and monocalcium ferrite $CaO.Fe_2O_3$ decreased to the small value of dicalcium ferrite $2CaO.Fe_2O_3$ with the nearly complete combination. Thus the combination to $2CaO.Fe_2O_3$ cannot be attained by heating at a temperature lower than 1,200 deg. C., even from a mixture of high lime content such as $2CaO : Fe_2O_3$, without a fluxing agent.

TABLE II.—SYNTHESIS OF CALCIUM FERRITES FROM THE MIXTURE $2CaO : Fe_2O_3$ $(2 : 1)$ WITH ADDITION OF 1 PER CENT. CALCIUM FLUORIDE, BY HEATING AT 1,110 TO 1,200 DEG. C. FOR ONE HOUR.

	CF_{2132}	CFF_{21101}	CF_{2130}	CFF_{21102}
Amount of added calcium fluoride, % ..	0	1	0	1
Temperature, deg. C...	1,100	1,100	1,200	1,200
Time, hours	1	1	1	1
Weight decrease, %	24.25	24.16	24.20	24.19
Amount of cal- ⌠Determined, % ..	0	0.49	0	0.51
cium fluoride ⌡Residual percentage ..	0	38.1	0	37.9
Free or uncombined lime, % ..	21.64	4.5	0.57	0.1
Free or uncombined ferric oxide, % ..	17.04	2.4	1.43	0.9
Amount of pro- ⌠ $CaO.Fe_2O_3$, % ..	25.2	8.0	0.2	0
duced calcium ⌡ $2CaO.Fe_2O_3$, % ..	36.1	84.6	97.8	98.5
ferrites Total, %	61.3	92.6	98.0	98.5
Molecular ⌠Total combined CaO .. ratio of ⌡Total Combined Fe_2O_3	1.72	1.95	2.02	1.98
Specific gravity of heated product	4.17	4.02	3.97	3.99

A proportion of 1 per cent. of calcium fluoride was added to the raw mixture $2CaO : Fe_2O_3$ $(2 : 1)$. This sample was heated at 1,100 to 1,200 deg. C. for one hour and the heated products were tested to study the effect of calcium fluoride on the combination of lime and ferric oxide in the same way as already

described.   The abridged results are given in Table II.   It is seen that the addition of 1 per cent. calcium fluoride is undoubtedly effective in combining lime and ferric oxide, as is seen in sample (CFF_{21101}), nearly completely to dicalcium ferrite $2CaO.Fe_2O_3$ even at 1,100 deg. C. or to nearly the same degree of the product (CF_{2130}) heated at 1,200 deg. C. without the addition of calcium fluoride. The presence of 1 per cent. of calcium fluoride is thus nearly equivalent to lowering the temperature 50 to 100 deg. C. at the heating temperature of 1,100 to 1,200 deg. C., which is nearly equal to the results observed in the studies of the synthesis of calcium aluminates in the presence of calcium fluoride.

The authors are studying the effects of other fluorides on the thermal syntheses of calcium silicates, aluminates, and ferrites of the important hydraulic compounds of Portland cement, aluminous cement, etc.

Solubility of Calcium Sulphate and Calcium Hydroxide.

INVESTIGATIONS have been carried out by P. Mecke (*Zement*, 1935, p. 764) on the solubility of calcium sulphate and calcium hydroxide in water and various solutions with the following results.

The solubility of $CaSO_4.2H_2O$ in water at 18 deg. C. is 203 mg. per 100 cc. ; at 100 deg. C. it is 175 mg. per 100 cc.   Ten grammes of plaster of Paris were mixed with 200 cc. of water and filtered after two minutes and again after 24 hours and 48 hours.   The results show that a supersaturated solution is formed.

	Sample I.	Sample II.
	mg. per 100 cc. water.	
After 2 minutes	815—826	828—830
,, 24 hours	256—236	289—261
.. 48 ,, ...	214—208	241—222

With ignited gypsum, 180 mg. went into solution at five minutes and 194 mg. at 24 hours.   In calcium chloride the solubilities were : 1 per cent. $CaCl_2$, 122 mg. ; 2 per cent. $CaCl_2$, 111 mg. ; 4 per cent. $CaCl_2$, 103 mg. per 100 cc. of solution. In concentrated ammonia solution the solubility was 60 mg. per 100 cc., and in a 1 : 1 solution 148 mg. per 100 cc.

The solubilities of $CaSO_4.2H_2O$ in solutions of various salts were found to be as follows (in mg. per 100 cc.): NH_4Cl : 1 per cent. solution, 354 mg. ; 2 per cent. solution, 568 mg. ; 4 per cent. solution, 646 mg.   NaCl : 2 per cent. solution, 520 mg. ; 4 per cent. solution, 592 mg. $(NH_4)_2SO_4$: 1 per cent. solution,

145 mg. ; 2 per cent. solution, 162 mg. ; 4 per cent. solution, 180 mg. ; 10 per cent. solution, 238 mg. Na_2SO_4 : 2 per cent. solution, 180 mg. ; 4 per cent. solution, 199 mg. In half normal HCl, the solubility was 950 mg. per 100 cc. ; in half normal H_2SO_4 it was 268 mg. per 100 cc. When $CaSO_4$ and $Ca(OH)_2$ are mixed together and treated with water, 162 mg. per 100 cc. only of $CaSO_4$ go into solution and 140 mg. of $Ca(OH)_2$. The effect of NaOH on the solubility is as follows :

	$Ca(OH)_2$.	$CaSO_4$.	NaOH.	Na_2SO_4.
	mg. per 100 cc.			
$CaSO_4$ + 1% NaOH	88	236	520	889
$CaSO_4$ + 0.2% NaOH	29	228	170	72
$CaSO_4$ + 0.2% NaOH + $Ca(OH)_2$ ..	38	233	170	80

This neglects the formation of the double salt $CaSO_4.Na_2SO_4$ and is therefore not quite accurate.

The solubility of $Ca(OH)_2$ in water was found to be 140 mg. per 100 cc. Quicklime can give somewhat supersaturated solutions on shaking with water ; 30 g. of CaO shaken with 200 cc. of water and filtered after a few minutes gave 190 mg. $Ca(OH)_2$ in 100 cc., but consistent results were not obtained and in one case 250 mg. per 100 cc. were dissolved.

The solubility of $Ca(OH)_2$ in solutions of sodium chloride rises at first with the concentration and then falls :

    2% NaCl solution   170 mg. $Ca(OH)_2$ per 100 cc. (162 mg.)
    4   ,,   ,,   182   ,,   ,,   ,,   ,,   (168 mg.)
    8   ,,   ,,   194   ,,   ,,   ,,   ,,   (179 mg.)
  10%   ,,   ,,   192   ,,   ,,   ,,   ,,   (174 mg.)
  26%   ,,   ,,   104   ,,   ,,   ,,   ,,   (90 mg.)

The second column gives the results obtained by gravimetric analysis and the third column those obtained by volumetric analysis ; no explanation of the divergence of the results has been found. One per cent. Na_2SO_4 solution dissolves 214 mg. and 2 per cent. Na_2SO_4 solution dissolves 300 mg. $Ca(OH)_2$ per 100 cc. A 1 : 1 ammonia solution dissolves 71 mg. $Ca(OH)_2$ per 100 cc. A 1 per cent. NaOH solution dissolves 21 mg. $Ca(OH)_2$ per 100 cc. $Ca(OH)_2$ forms various oxychlorides with solutions of $CaCl_2$ which are discussed in a paper by the author in *Tonind. Zeit.*, 1934, Nos. 57 to 59.

In sugar solutions the solubilities are as follows : 1 per cent. solution, 158 mg. ; 2 per cent. solution, 240 mg. ; 4 per cent. solution, 386 mg. per 100 cc. A 1 per cent. carbolic acid solution dissolves 318 mg. per 100 cc. The results, except where otherwise stated, were obtained at 18 deg. C.

Integral Waterproofers.

THE following notes on integral waterproofers are taken, by permission, from an article by Mr. H. M. Llewellyn, B.Sc., A.I.C., dealing generally with the waterproofing of building materials in *Chemistry and Industry*.

The various waterproofing materials which are used in admixture with mortar and concrete may be divided into two classes, viz. (1) materials intended to reduce the permeability of the mass, but not primarily intended to alter its rate of setting, (2) materials which are used specifically to accelerate the setting of Portland cement.

The most obvious way to make concrete impervious to the passage of water is to reduce the void space to the minimum ; actually by exercising due care in grading of aggregates, proportioning and mixing, and in control of the amount of gauging water and the method of placing, concrete can be made sufficiently impervious for all ordinary requirements. The conditions of ordinary practice, however, do not always allow the fullest control in all these respects, and the use of waterproofing additions is intended to remedy possible deficiencies. For renderings and jointing mortars lean mixes are often necessary in order to avoid excessive shrinkage. Usually, therefore, they are more or less permeable, but the addition of a waterproofer may considerably reduce the rate at which water is absorbed, especially when the pressure of water is only slight or intermittent. Renderings which have to withstand continuous high pressures require special treatment, which will be referred to later.

Integral waterproofers are marketed in the form of powders, pastes, or liquids. Some are simply finely-ground inert substances such as chalk or talc, intended to improve the plasticity of the mix and reduce void space. Usually, however, these powders are employed in conjunction with substances of a hydrophobic character, e.g., calcium or aluminium soaps. Liquid waterproofers frequently contain substances capable of reacting with a second solution, or with the cement to form an insoluble product. Examples of this type are solutions of alkali silicates, calcium chloride, zinc sulphate, and ordinary soap. The two former substances in concentrated solution accelerate the setting of Pcrtland cement and are used specifically for this purpose. Another " active " addition which is sometimes used is a mixture of iron filings and ammonium chloride. Here the intention is that the iron in contact with the salt should rust and in so doing expand and fill the voids. Iron filings when used alone will not rust in the interior of the mass, and hence would be classed as an inert filler. The majority of waterproofers, however, are dependent upon definite water repellent properties, and include a wide variety of substances comprising metallic soaps, oils, fats, waxes, resins, rubber, and bituminous materials.

As with surface waterproofers, there appear to have been few attempts to evaluate the various types of integral waterproofer on a comparative basis ; doubtless this is due to the fact that nearly all are proprietary articles and hence usually of secret composition. Investigations at the U.S. Bureau of Standards included fifty samples of integral waterproofers, both proprietary and otherwise.

The materials were classified according to their composition under six categories. Specimens of 1 : 3 : 6 Portland cement concrete prepared both with and without the waterproofing additions were tested for permeability (under a pressure of 20 lb. per square inch), absorption (on immersion), and compressive strength.

In these tests it was found that calcium chloride had little effect on either permeability or absorption, but increased the compressive strength. The use of such materials as soap, silica, and aluminium chloride in conjunction with calcium chloride did not reduce permeability, but a mixture of calcium chloride and soap reduced absorption without, however, increasing strength. Soap alone increased permeability and reduced absorption and strength ; hydrated lime and soap had a similar effect. Finely-divided materials (e.g., diatomaceous earth, bentonite, etc.) reduced permeability, increased strength, and did not affect absorption. Materials such as cellulose, wax, fluoscilicates, naphthalene, vaseline, and coal tar did not reduce permeability but reduced both compressive strength and absorption. The results as a whole therefore appeared to show that such integral waterproofers as were tested were ineffective in reducing the permeability of concrete to water under pressure, although some materials reduced the rate of absorption of the specimens on simple immersion.

White and Bateman[1] report more favourably on the effect of soaps on the permeability of concrete. Comparatively few integral materials have been tested at the Building Research Station, but tests which have been made substantially confirm the general conclusion already stated.

In view of this, it is considered that certain integral waterproofers can usefully be employed to help resist the penetration of damp, but that in situations where mass concrete will be subject to a fair pressure of water reliance should not be placed primarily on the efficacy of a waterproofer to prevent percolation, but rather every means should be taken to ensure that the concrete shall have a minimum permeability. It is claimed for some products that they assist materially to this end when the conditions are those normally prevailing in practice. If so, the main factor will be that of cost ; it will be necessary to consider whether the benefit likely to accrue from the waterproofing addition will be commensurate with the extra expenditure involved, or whether the additional cost could not be expended with equal or greater advantage in improving the quality of the concrete.

The position with regard to the use of integral waterproofers in cement renderings is somewhat different from that outlined. It has already been shown that such additions to a pervious concrete may reduce the absorption under a low head, and the same applies to mortars. In renderings applied to the outside of buildings, however, the penetration of moisture is liable to occur not so much by reason of the permeability of the mass as by way of the cracks which so frequently develop as the result of shrinkage. The addition likely to be of greatest benefit, therefore, would be one which would reduce the tendency to shrinkage. No evidence is yet available as to whether any waterproofers have

[1] White and Batemen, *Proc. Am. Con. Inst.*, 1926, **22**, 535.

such an effect or not.   In cases where a waterproof rendering is required to be applied to a surface already damp and subject to low hydrostatic pressure, e.g., the walls of basements on wet sites, there is often considerable difficulty in making an ordinary rendering adhere.   It is here that a waterproofer of the accelerator type may be of great utility.   Solutions of calcium chloride (and certain other chlorides) and also of alkali silicates both possess the property of accelerating the setting of Portland cement.   When used in proper concentration with neat cement or rich cement mortars, they produce setting within a few minutes, and by taking advantage of this fact a surface can be rendered with an impervious coating even against quite considerable water pressure.

One final aspect may be considered and that is that many of the specialist firms who apply proprietary waterproof renderings get very satisfactory results. This may quite possibly be due not so much to the efficacy of the waterproofer used as to the technique and skill of the operatives.   Where waterproofers are employed by the ordinary builder there is a strong psychological factor involved —which may often make for success ; the operative has minute instructions on the container of the waterproofing medium, and the mixing and proportioning, as well as the preparation of the surface to be rendered, are carefully carried out.